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QUALITATIVE DIFFERENTIAL THERMAL ANALYSIS OF AMMONIUM NITRATE, AMMONIUM PERCHLORATE, POTASSIUM NITRATE AND POTASSIUM PERCHLORATE

JOHN V. SMITH

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THESIS

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OF AMMONIUM NITRATE, AMMONIUM PERCHLORATE,

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by

John V. Smith
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John V. Smith
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Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN
CHEMISTRY

United States Naval Postgraduate School
Monterey, California

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ABSTRACT

Differential Thermal Analysis Curves (thermograms) were made of ammonium nitrate, ammonium perchlorate, potassium nitrate, and potassium perchlorate over the temperature range, 25° - 400°C by Lt. John V. Smith, U. S. N., at the UnitedStates Naval Postgraduate School. A knowledge of the temperatures of the phase transitions and of the decomposition phenomena associated with these compounds when they undergo heating is valuable as these compounds are often components of pyrotechnics and propellants. The differential thermal analysis apparatus used employed thermistors as sensing elements instead of thermocouples because of the formers greater sensitivity. Results are compared with previous work in this field. Selected portions of thermograms for each compound as well as photographs of the apparatus are included.

The writer wishes to express his appreciation for the assistance and encouragement given him by Professor Carl Hering of the United States Naval Postgraduate School in the pursuit of this project, and to Messers. Jack M. Pakulak and William M. Ayers of the Naval Ordnance Test Station, China Lake, California, for their assistance in the construction of the apparatus and instruction in the techniques of differential thermal analysis.

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1. Introduction

The phase transformations and decomposition phenomena that occur when inorganic oxidants are heated are of particular interest since these compounds are often used in pyrotechnics and solid propellants. These changes are of particular importance since they (a) involve dimensional changes in the structure of the compounds, and (b) serve as heat sources or heat sinks depending on whether the changes are exothermic or endothermic.

Differential thermal analysis has for many years been extensively used by mineralogists in the study of clays, minerals, and soils, etc., and it appeared to be an excellent method for studying the thermal decomposition of inorganic oxidants. Some isolated work has been done in the field, for example by Gordon and Campbell (3) of the Pyrotechnics Chemical Research Laboratory, Picatinny Arsenal, Dover, New Jersey. Recently, Pakulak and Leonard (9) of the Naval Ordnance Test Station, China Lake, California demonstrated the effectiveness of a simple and very sensitive differential thermal analysis apparatus which used thermistors instead of therocouples as sensing elements. Because of its great sensitivity this type of apparatus was chosen for the project.

The objective of the project was twofold. First to build, test and calibrate the thermistorized apparatus and secondly, to analyze various compounds with it. The compounds chosen were ammonium nitrate, ammonium perchlorate, potassium nitrate and potassium perchlorate as all are extensively used in pyrotechnics and propellants. The temperature range of the study was from room temperature to 400°C, the upper limit being imposed by the physical limitations of the apparatus.

2. Theory

The following discussion is concerned primarily with those aspects of differential thermal analysis which apply to the apparatus used in this project. For an extensive treatment of differential thermal analysis, both qualitative and quantitative, the reader is referred to Smothers and Chiang (11) "Differential Thermal Analysis: Theory and Practice". An additional valuable feature of this book is an extensive bibliography of publications and technical articles concerning differential thermal analysis.

Differential thermal analysis hereinafter called DTA is essentially a refinement of the classical procedure of studying phase transformations by use of time temperature curves obtained from uniform heating or cooling of a substance. In DTA the material under study and an inert material are heated side by side with both the temperature of the sample and the temperature difference between the sample and the inert material being recorded. It is assumed that when the sample is undergoing no transformation the temperature of both sample and inert material are the same. When any change in the sample occurs which involves either the release or the absorption of heat, then a temperature difference will result between the sample and the inert material. When a temperature difference versus time curve is made, phase transformations, decompositions, etc., appear as peaks or deflections from the base line. For examples see figures 7 through 17.

An analysis of these peaks with regard to the factors which determine their size, shape, and position is exceedingly complex. However, from a qualitative point of view two points on the peaks are significant, the start of the peaks and the peak's maximum. The sample temperature

corresponding to the initial inflection of the peak is the temperature at which the transformation is first evident. In the case of crystalline inversions it can be considered the transition temperature. The sample temperature corresponding to the peak's maximum has been shown by H. E. Kissinger (5) of the National Bureau of Standards, Washington, D. C., to be the temperature at which the reaction rate is a maximum. This is true, however, only when the heating rate of the inert material is constant.

In the present project the sample and inert materials were placed in identical 75 mm test tubes which were then placed in identical holes machined in an aluminum block (see figure 6). The block was next placed in a furnace where an essentially uniform heating rate was applied (see figure 3). Into each test tube was placed a thermistor which acted as a temperature sensing element, (see figure 5). A thermistor is an excellent temperature sensing element as very small changes in temperature result in very large changes in resistance. With the two matched thermistors placed in adjacent arms of a Wheatstone bridge, any unbalance resulting from a temperature difference will result in a signal that can be fed to a recorder.

In order that one can be confident that recorded peaks actually do represent exothermic or endothermic changes a basic assumption must be made, that the temperatures measured by the two thermistors are essentially equal when no transformations are taking place. Since these temperatures depend upon the rate of heat transfer into the test tube system (consisting of test tube, sample or inert material as the case may be, and the thermistor probe) for them to be equal would imply equal thermal diffusivities. Thermal diffusivity α is defined as

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$$\alpha = \frac{K}{\rho C_p}$$

where K is the thermal conductivity, ρ is the density and Cp is the specific heat at constant pressure. For the two test tube systems used the thermal diffusivities are practically equal since they differ physically only in the relative amounts of the sample and inert material. The inert material used is one gram of very fine glass beads approximately $\frac{1}{2}$ micron in diameter. The sample consists of the substance under study intimately mixed with one gram of glass beads with a dilution factor roughly ten to one, ie., one gram glass beads to one tenth gram of substance under study. Hence, it can be seen that the two test tube systems are practically equivalent. Any actual difference in the thermal diffusivities are corrected by appropriate balancing of the bridge circuit at beginning of run. Calculations based on experimental evidence show that the temperature difference that exists when no transformations are occuring is only of the order of from one tenth to one hundredth of a degree centigrade.

One final point must be considered. In the present apparatus the temperature of the sample is not actually recorded. Rather the temperature recorded is that given by a thermometer placed in a third test tube packed with glass beads and identically mounted in the aluminum block. It is assumed that this temperature is equal to that of the sample, an assumption consistent with the accuracy of temperature measurement in the present apparatus. Even when a differential temperature exists the difference seldom exceeds one degree centigrade.

3. Apparatus

The apparatus used in this project was an adaptation of that described by Pakulak and Leonard in reference (2). A block diagram of the assembled major components is shown in figure 2 and a photograph in figure 3.

Basic parts of the apparatus are the furnace, bridge circuit, recorder, decade voltage divider, aluminum block, thermistors, thermometer, three volt D.C. battery, vacuum tube multimeter, and variable autotransformer. The recorder used was a Varian G-10 graphic recorder calibrated for ten millivolts full scale deflection. Chart speed was one inch per minute. The base line was adjustable and both positive and negative signals were recorded. The decade voltage divider was used to reduce the signal input to the recorder when necessary and was a type 654-A manufactured by the General Radio Company. Table #1 below gives the percentage signal input passed for various settings of the voltage divider.

SETTING	PERCENT SIGNAL PASSED
1.0	100
.9	90
.8	79
.7	68
.6	57
.5	46
.4	36
.3	25
.2	14
.1	3

Table #1

Voltage Divider Calibration

The variable autotransformer was a Variac model V10, 115 volt, 10 amp., 50-60 cycle, manufactured by the General Radio Company. It was

used to control the furnace heating rate. The vacuum tube voltmeter utilized was a Simpson model 303. The meter was used to measure the voltage across the bridge circuit. The direct current voltage across the bridge was supplied by a Burgess, three volt, type 4F2H, general utility battery. The thermometer manufactured by Fisher had a 76 mm immersion, a range of -10° to 400°C, and is calibrated in one degree increments. The construction of the furnace, aluminum block, bridge circuit and thermistor probes will be described in succeeding paragraphs.

Furnace and Aluminum Block. The case of the furnace was fabricated from a five gallon can with the top cut off. It was a cylinder 14 inches high and 11 inches in diameter. The heating element of the furnace was made using a 3 1/16 inch interior diameter furnace muffle, 6 inches high, wound with #18 nichrome wire. The element was rated at 1200 watts. All extra space in the furnace was packed with crushed fire brick as insulation. The top cover was made of $\frac{1}{4}$ inch transite with a hole cut the size of the muffle in order to provide for easy removal of the aluminum block. A transite board was placed across the bottom of the heating element to give a firm base for the block to rest on.

The aluminum block was made from round stock turned down on a lathe to 3 1/32 inches diameter. Its length was 5 inches. Three holes 120 degrees apart, with their centers 3/4 of an inch from the block's center were drilled to accommodate the 10 by 75 mm pyrex test tubes. The holes were 70 mm deep and $10\frac{1}{2}$ mm in diameter. An eye was placed in the center of the top of the block to facilitate removal (see figure 6).

Bridge Circuit. The bridge circuit was constructed in accordance with the circuit diagram of figure 1. Precision components were used

throughout to insure stability. The bridge consisted of one megohm thermistors and their parallel shunts located in adjacent arms. Two shunts were provided one of 50,000 ohms and one of 2000 ohms. The bridge could be operated in three ways, a) thermistors alone, b) thermistors with 50,000 ohm shunts and c) thermistors with 2000 ohm shunts. Table #2 gives the values of resistance versus temperature for all three conditions.

TEMPERATURE °C	THERMISTOR (ohms)	THERMISTOR WITH 50K SHUNT (ohms)	THERMISTOR WITH 2K SHUNT (ohms)
25	900,000	47,400	2,000
50	293,000	42,700	1,985
75	102,000	33,600	1,960
100	37,700	21,500	1,900
125	16,600	12,500	1,785
150	8,330	7,150	1,610
175	4,320	3,960	1,370
200	2,320	2,200	1,070
225	1,320	1,270	795
250	820	806	582
275	519	514	412
300	350	348	298
325	239	238	214
350	164	164	152
375	118	118	111
380	112	112	106
385	106	106	101

Table #2

Thermistor Resistance Versus Temperature

During this project, the thermistors with 50,000 ohm shunts were used exclusively as the maximum permissible source resistance for the Varian recorder is 50,000 ohms. Table #3 shows the relative strength of signals generated by a 5 degree temperature difference at selected temperatures for the various thermistor and shunt combinations.

TEMPERATURE °C	THERMISTORS ALONE	THERMISTORS WITH 50K SHUNTS	THERMISTORS WITH 2K SHUNTS
50	560	70	1
100	340	260	30
200	290	240	130
300	180	180	160
380	140	140	125

Table #3

A comparison of relative signal strengths generated when a 5 degree temperature difference existed at different temperatures for the various thermistor and shunt combinations.

The two resistors in the opposing arms were 1000 ohms each. A 50 ohm, 10 turn helipot was provided for a balance control of the bridge. A picture of the bridge (less thermistors) is shown in figure 4.

Thermistor Probes. A thermistor probe assembly consisted of three parts, a) a two inch glass walled one megohm thermistor, b) the pyrex probe and c) a special 10 by 75 mm pyrex test tube. The glass walled thermistors were manufactured by the Victory Engineering Company, Union, New Jersey. (Stock number 61A1). As the thermistors were not matched when purchased it was necessary to secure a number of them, calibrate them and thus find a matched pair. The method of calibration was as follows. The DTA apparatus itself was utilized by recording the voltage signals generated (at constant temperatures 25°C, 50°C, 100°C, 150°C, etc.) when one thermistor was used as a reference and each of the other thermistors was compared with it. The signals generated were proportional to the difference in resistance that existed between the two thermistors at some specific temperature. The magnitudes of the signals were then plotted against temperature and the resulting curves were compared. For example, if two thermistors when compared against the reference

thermistor at 100°C each gave rise to a signal of 10 millivolts one would assume they were matched at that temperature. Hence if two curves were nearly coincident from 25 - 400°C, then it was reasonable to assume the two thermistors were closely matched. Next, if one found a promising pair, it was necessary to make a blank run to determine if they were actually usable. This author when calibrating thermistors was able to match only three separate pairs out of a total of 25 individual thermistors.

The pyrex probes (see figure 5) into which the thermistors were placed were necessary for two reasons. First, the probe properly positioned the thermistor in the test tube and, secondly, it helped protect the delicate thermistor leads from being attacked by volatile decomposition products. The probe was 72 mm in length and consisted of a 3.5 mm outer diameter pyrex tube, 72 mm long and sealed at the bottom, surrounded by an 8 mm outer diameter pyrex test tube, the two being sealed together at the probes midpoint. The inner tube protected the thermistor and the outer tube fitted snugly into the 10 by 75 mm test tube to give proper positioning. The space between the inner and outer tubes was filled with granulated asbestos insulation. Once the thermistor was installed in the probe, its leads were separated and the top of the probe was sealed with electric resistor cement.

The 10 by 75 mm test tubes were modified by making a pin-hole at the midpoint. This was done in order to let gases escape which would otherwise build up a pressure and shift the position of the probe.

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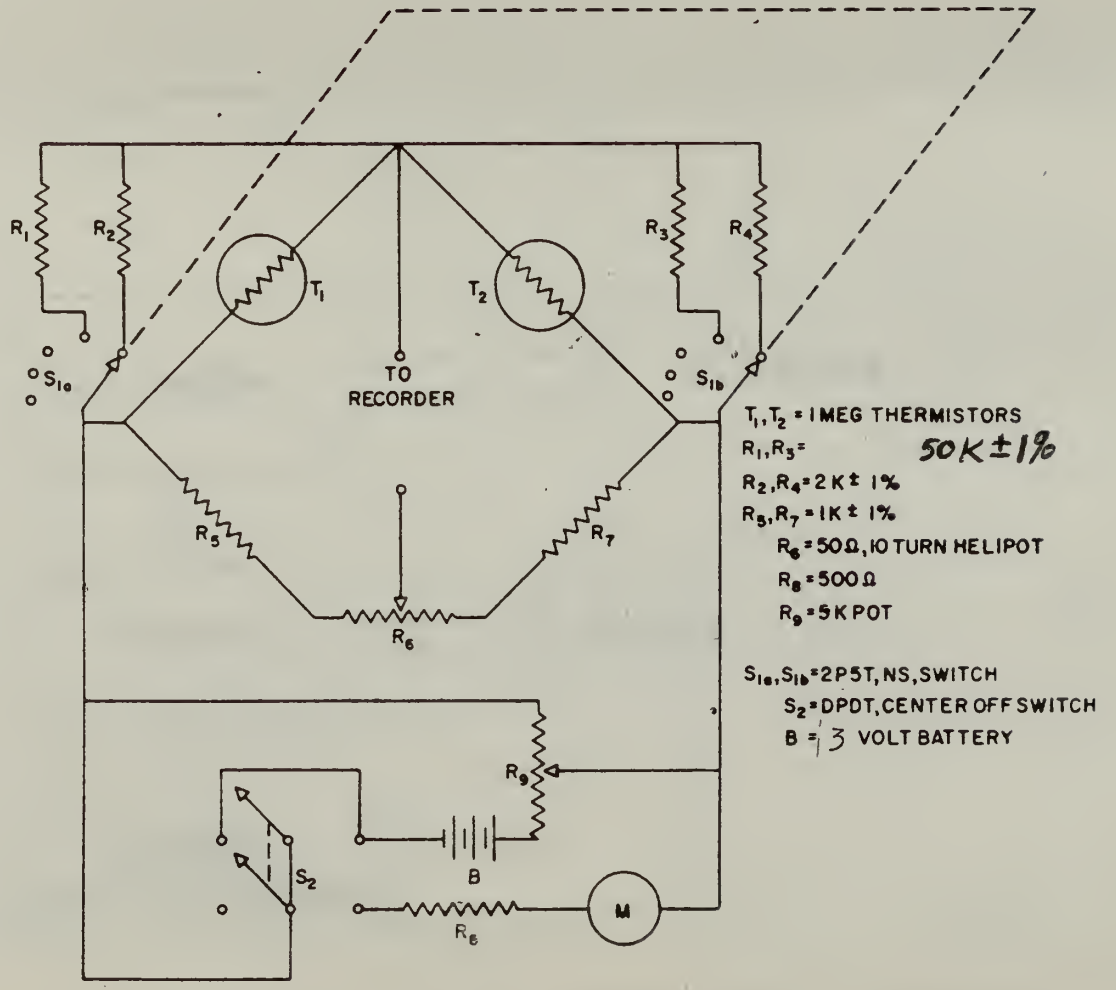

Figure 1 - Bridge
Circuit Diagram

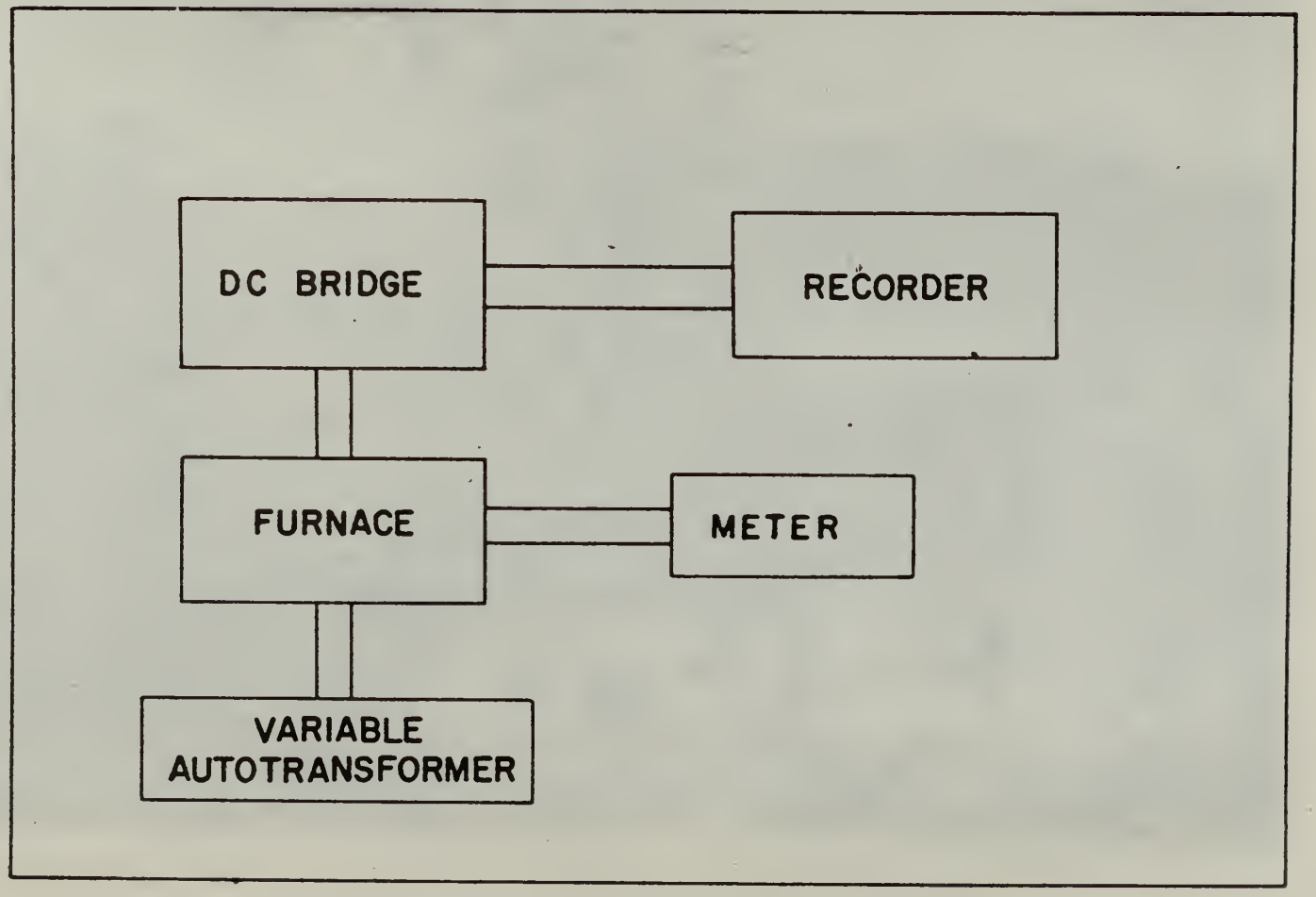

Figure 2 - Block Diagram

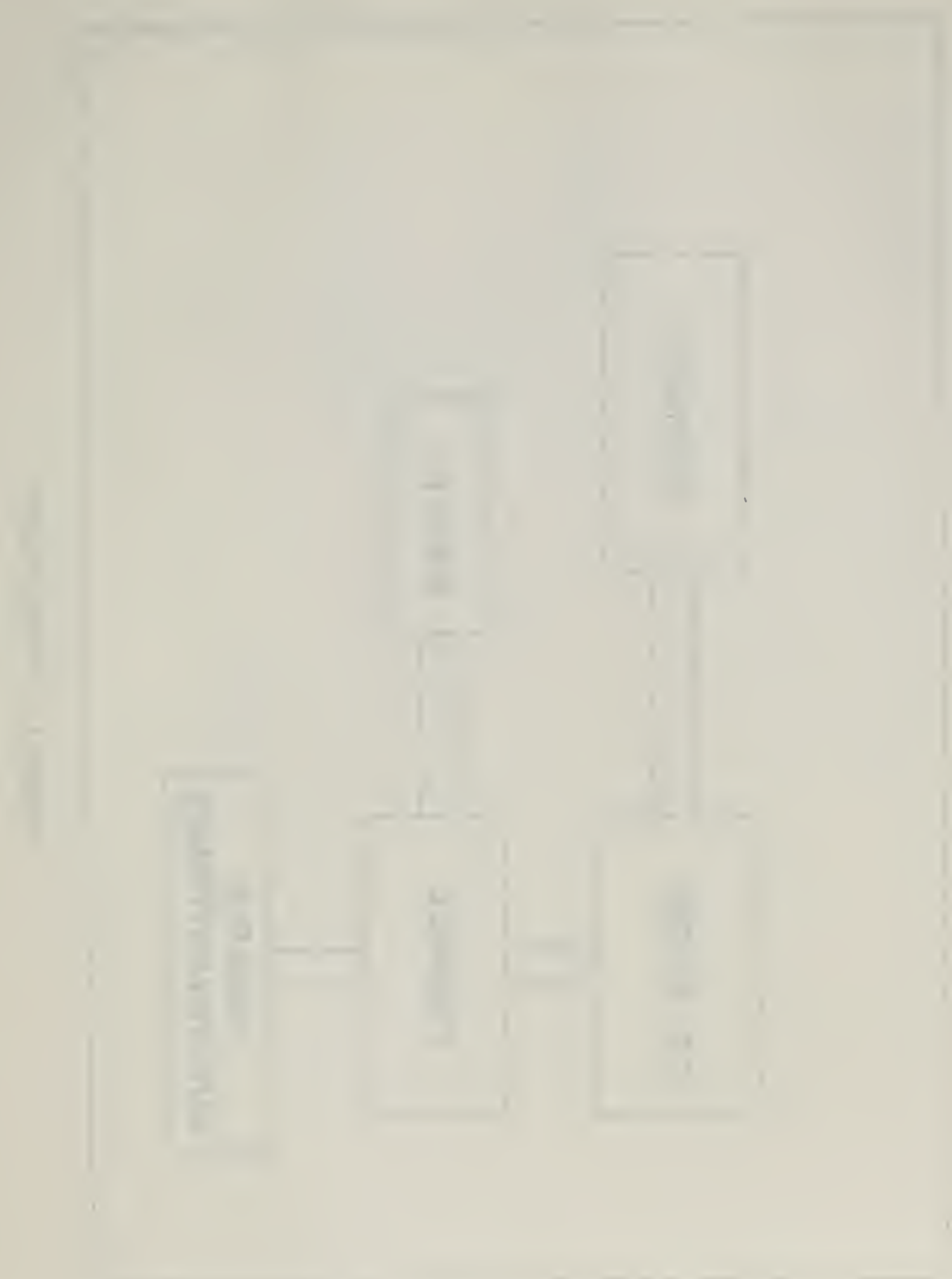

Figure 3 - DTA Apparatus

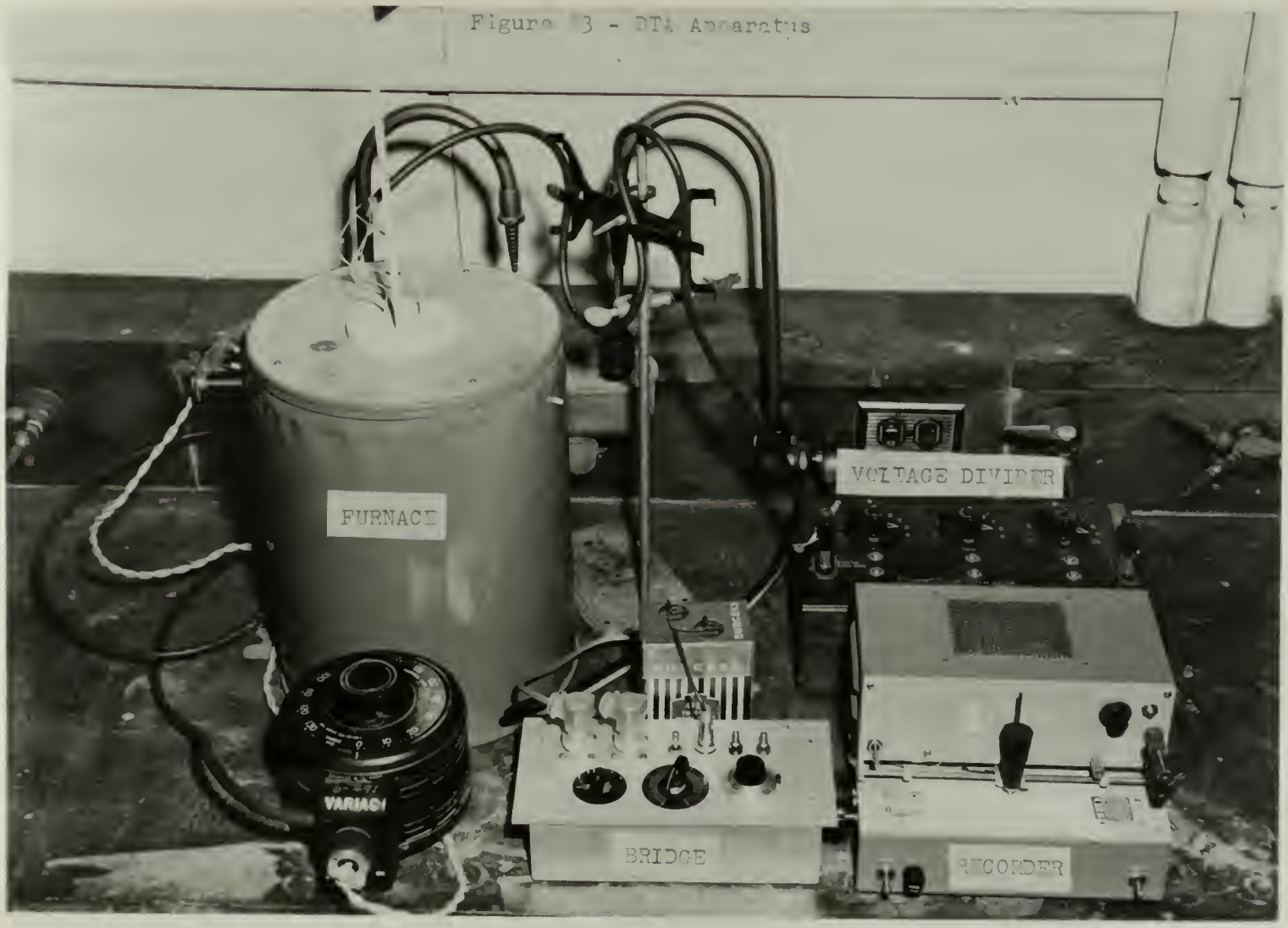

Figure #4 - Bridge

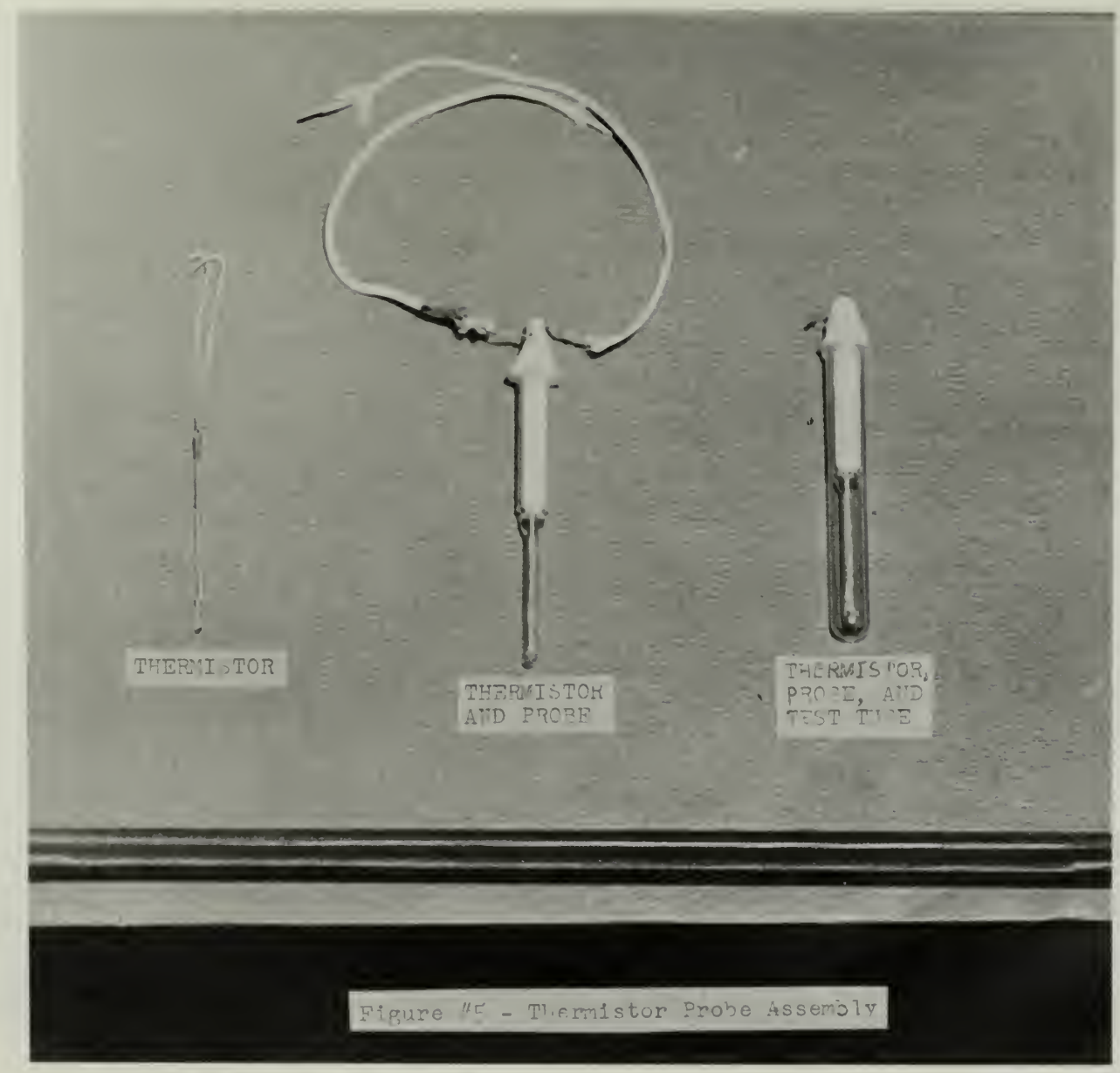

Figure #5 - Thermistor Probe Assembly

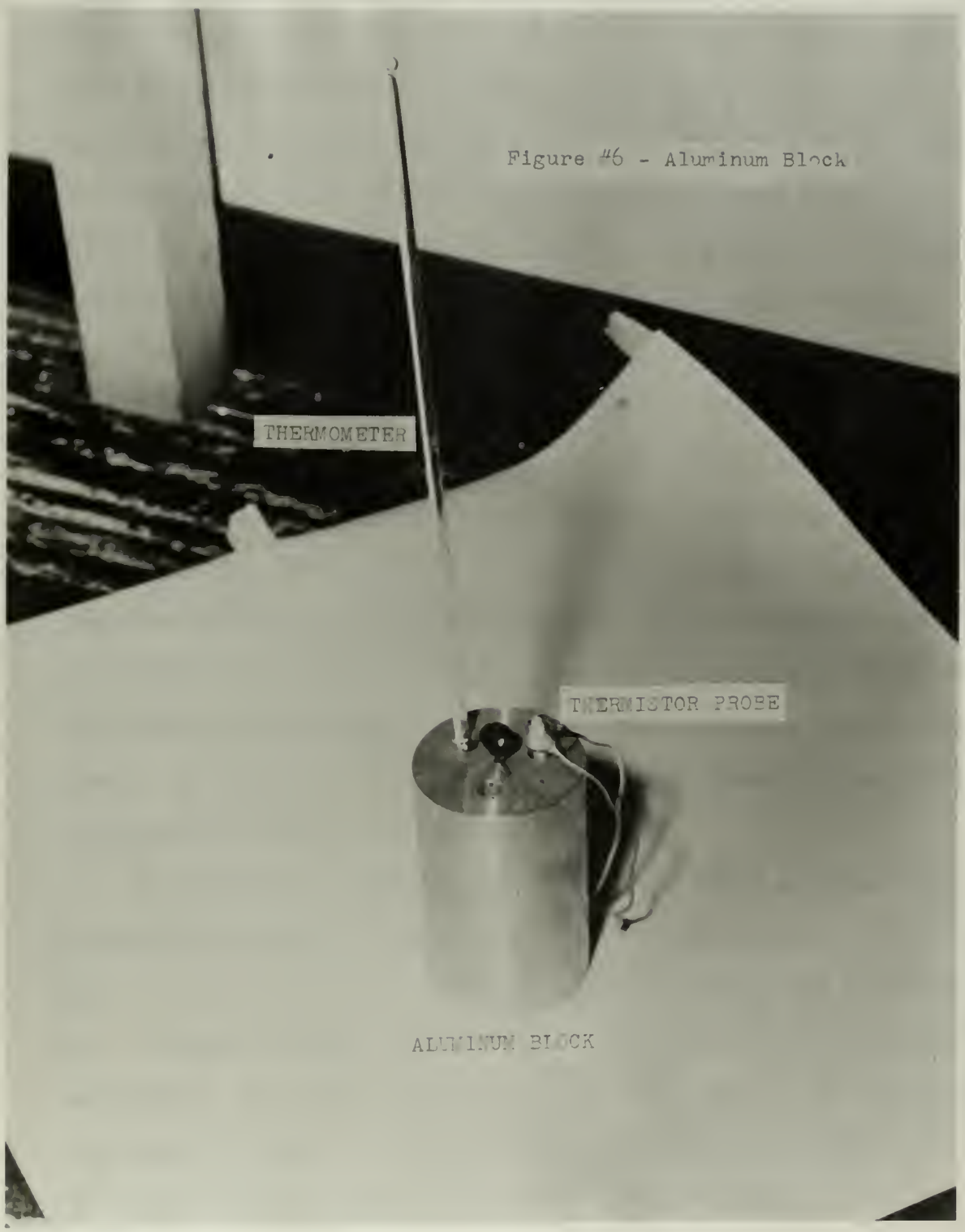

Figure #6 - Aluminum Block

4. Procedure

The chemicals in this study were commercially prepared as follows: ammonium nitrate (B&A, granular, reagent grade); ammonium perchlorate ("Baker's Analyzed"); potassium nitrate (B&A, crystal, reagent grade); potassium perchlorate (B&A, crystal, reagent grade). Each reagent was ground fine with a mortar and pestle and, with the exception of ammonium nitrate, dried in the oven for twenty-four hours at 110°C. In addition, portions of each chemical were recrystallized from distilled water, and with the exception of ammonium nitrate, dried for forty-eight hours at 110°C. All reagents were then kept in dessicators.

Each run was made in the following manner. One gram of glass beads was weighed out on the analytical balance and placed in a 10 by 75 mm test tube. Next, the required amount of reagent was weighed on the balance and then transferred to the same test tube. The glass beads and sample were thoroughly mixed with a spatula, taking care that the chenical was pulverized in the process. Following this the thermistor probe was inserted and the test tube assemply placed in the aluminum block. The other test tube containing the other thermistor and one gram of glass beads was similarly placed.

The thermistor leads were connected to the bridge and the bridge subsequently balanced so that a zero signal would be fed to the recorder. At this time the actual voltage across the bridge would be recorded. A suitable setting usually 1.0 or .30, would be made on the voltage divider, the variac turned on and the run started. The chart speed was always 1" minute. In order to hold the heating rate to 2° - 3°C per minute the following variac settings were made during a run:

SETTING	TEMP - °C
40	25
45	113
50	199
55	312

Temperatures were taken as often as desired and recorded directly on the chart paper. Throughout the run any notes of interest were made on the chart and in the case of ammonium nitrate and ammonium perchlorate the results of testing the fumes with moistened litmus paper were also noted.

At the completion of a run the voltage across the bridge would again be taken. The reason for doing this was to keep a check on the battery. For a fresh battery the voltage would be 3.0 volts at the start of a run (25°C) and would drop to 2.5 volts at the end of a run (400°C). During a run it would often be necessary to shift the base line and or reduce the signal strength in order that the recording pen not go into the stops. This would occur during strong endothermic or exothermic transformations.

The only serious mechanical trouble that occured during the course of the study was occasional erratic pen behavior. This was traced to the thermistor leads, which, after a certain number of runs would fail to make good contact. This was remedied by crimping the leads prior to each run.

5. Data

A total of 21 runs were made during this project, each taking approximately three hours. The first three were calibration runs made in order to check the thermistor drift. These blank runs were made by having both thermistors in a gram of glass beads. Over the maximum range of the apparatus (25°- 400°C) a long 15 foot trace was made with a very gradual slope deviating at maximum only 3 millivolts from the zero base line. From this it was learned that the thermistors were an excellent match.

The final 18 runs were made with the sample reagents as follows:

Ammonium nitrate	6 runs
Ammonium perchlorate	5 runs
Potassium nitrate	4 runs
Potassium perchlorate	3 runs

The summary of pertinent data is contained in tables 4 through 7. All temperatures are as recorded during a run (ie., uncorrected) and are those temperatures occurring at the start of a peak and at the peak's maximum. Figures 7 through 17 are representative full scale thermograms for all the reagents studied. These thermograms contain all the temperature regions in which endothermic or exothermic peaks occurred.

Run	Date	Size Sample (gram)	Temp. Range °C	Type Peak	Initial Temp. °C	Maximum Temp. °C
1	28 Jan 60	.0800 Unrecrystal-lized	25-320	Endothermic	39	44
				"	89	96
				"	128	131
				"	156	168
				Exothermic	245	259
				Endothermic	278	300
2	3 Feb 60	.1600 Recrystal-lized	25-390	Endothermic	36	41.5
				"	53	55.5
				"	87	91
				"	128	132
				"	143	157
				Exothermic	237	270
				Endothermic	282	299
3	9 Feb 60	.1600 Recrystal-lized	25-230	Endothermic	53	56
				"	88	90
				"	128	131
				"	150	168
4	13 Feb 60	.1600 Unrecrystal-lized	26-347	Endothermic	39	43
				"	88	96.5
				"	128	131
				"	150	168
				Exothermic	240	254
				Endothermic	280	302
5	22 Mar 60	.1600 Recrystal-lized	28-324	Endothermic	38	NOT DETERMINED
				"	54.5	57
				"	89	92
				"	129	133
				"	154	170.5
				Exothermic	230	254
				Endothermic	281	303
6	24 Mar 60	.1600 Recrystal-lized	27-331	Endothermic	38	48
				"	55.5	57
				"	89	92
				"	129	133
				"	154	171
				Exothermic	240	255
				Endothermic	281	303

Table #4

Ammonium Nitrate - Summary of Data

Run	Date	Size Sample (grams)	Temp. Range °C	Type Peak	Initial Temp. °C	Maximum Temp. °C
1	19 Mar 60	.0588 Recrystal-lized	26-352	Endothermic	243	246
2	20 Mar 60	.0588 Unrecrystal-lized	26-400	Endothermic Exothermic	243 378	245 389
3	21 Mar 60	.0588 Recrystal-lized	26-400	Endothermic Exothermic	243 378	246 391
4	22 Mar 60	.0588 Recyrstal-lized	95-400	Endothermic Exothermic	243 378	247 391
5	25 Mar 60	.0588 Unrecrystal-lized	94-400	Endothermic Exothermic	243.5 379	246.5 391

Table #5

Ammonium Perchlorate - Summary of Data

Run	Date	Size Sample (grams)	Temp. Range °C	Type Peak	Initial Temp. °C	Maximum Temp. °C
1	19 Feb 60	.1011 Unrecrystal-lized	25-205	Endothermic	130	134
2	15 Mar 60	.1011 Unrecrystal-lized	25-362	Endothermic "	130 320	134 334.5
3	15 Mar 60	.1011 Recrystal-lized	27-339	Endothermic "	130.5 -	134 334
4	16 Mar 60	.0505 Recrystal-lized	26-365	Endothermic "	131 320	134 334

Table #6

Potassium Nitrate - Summary of Data

Run	Date	Size Sample (grams)	Temp. Range °C	Type Peak	Initial Temp. °C	Maximum Temp. °C
1	17 Mar 60	.1385 Recrystal-lized	26-328	Endothermic	302	306
2	18 Mar 60	.0692 Unrecrystal-lized	23-320	Endothermic	301.5	304.5
3	18 Mar 60	.0692 Recrystal-lized	197-320	Endothermic	301.5	304.5

Table #7

Potassium Perchlorate - Summary of Data

6. Results

General. The two objectives of this project were achieved. First the apparatus was constructed and found to perform according to expectations. Second, detailed thermograms were obtained of the four reagents under study. Unfortunately due to a change in the thermometer at some point in the study temperatures recorded may be in error by three degrees, probably high.

Prior to commencing any runs the thermometer had been calibrated against the ice point, boiling point of water and condensation point of diphenylamine. No detectable errors were noted. At the completion of the runs the thermometer was recalibrated and found to be three degrees too high. The cause of this has not been determined nor has it been possible to tell whether the shift happened gradually or at one specific time. One possible explanation is that stresses may have been present in the mercury bulb and these were relieved by the bulb's being annealed for many hours at high temperatures. By examining the thermograms which were made during the present series it is felt that the shift occurred during the calibration runs and prior to the data runs. Thus a $-3^{\circ}C$ correction was applied and these are the temperatures tabulated in tables 8 through 10.

Tables 8 through 10 represent the best estimate of transition temperatures made by considering all the thermograms and by applying the 3 degree correction factor. In addition tables 8 and 9 contain known transition temperatures as compiled by Rossini and Associates (10) of the National Bureau of Standards.

In succeeding paragraphs the results obtained for each compound studied will be discussed.

Formula	DTA Transition Temp. °C	Reported Transition Temp. (5) °C	Crystalline Modification
NH_4NO_3	35	32.1	Rhombic II-I
	51	See Text	Rhombic II-Tetragonal
	85	84.2	Rhombic I-Tetragonal
	125	125.2	Tetragonal-Cubic
NH_4ClO_4	240	240	Rhombic-Cubic
KNO_3	127	127.7	Rhombic-Trigonal
$KClO_4$	299	299.5	Rhombic-Cubic

Table #8

Tabulation of Crystalline Transitions

Formula	DTA Fusion Range °C Initial Temp.	Peak Maximum	Reported Fusion Temp. (5)
NH_4NO_3	150	166	169.6
KNO_3	317	331	337

Table #9

Tabulation of Fusion Transitions

Formula	Exothermic Range °C Initial Temp.	Peak Maximum	Endothermic Range °C Initial Temp.	Peak Maximum
NH_4NO_3	234-242	251-256	275-278	297-300
NH_4ClO_4	375-376	386-388		

Table #10

Tabulation of Decomposition Temperatures

Ammonium Nitrate. Ammonium nitrate gave the most complex thermogram of any compound, (see figures 7 through 12). Run #2 was not considered when making up tables 8 through 10 as the recrystallized sample had not been in the dessicator long enough to sufficiently dry it (only 24 hours), hence the run was not representative.

The temperatures for the crystalline transitions agreed closely with literature values (see table #8). The first transition from rhombic II to rhombic I appeared as a broad, slight endotherm and in run #3 could not be detected at all. The transition noted at 51° occurred in all four runs where recrystallized samples were used, but was not present in runs where the unrecrystallized samples were used. This transition at 51° is assumed to be rhombic II to tetragonal as Alekseenko and Boldyrev (1) and Morand (8) both previously noted it. Apparently both the tetragonal and rhombic I forms must coexist as the transition rhombic I to tetragonal occurred in every thermogram. Below is a comparison of the crystalline transition temperatures noted in this work with that of other DTA.

TRANSITION	THIS WORK	GORDON AND CAMPBELL (3)	ALEKSEENKO AND BOLDYREV (1)	MORAND (8)
Rhombic II-I	35	33	32	32
Rhombic II-TET	51		50	55
Rhombic I-TET	85	89	85	82
Tetragonal-Cubic	125	129	125	125

Fusion occurred over a broad range peaking at 166°C, a temperature about 4° lower than the literature value. Gordon and Campbell (3) reported 170°C as the temperature of fusion from visual observation.

The decomposition of NH_4NO_3 was detected by DTA from about 234°C

to 325°C. A pronounced exothermic peak occurred at about 253°C and a pronounced endothermic peak at 298°C. By testing the atmosphere above the sample tube with moistened litmus decomposition was detected down to 197°C. The litmus registered basic throughout with a pH of 8. White fumes were visible at 278°C disappearing at 325°C. Keenan (4) investigated by DTA the decomposition from 190° to 300°C at a 2°C/min. heating rate and observed a broad exotherm from 190°C peaking at 270°C. No endotherm was noted. He assumed the decomposition products to be N_2O, H_2O and some N_2. It should be noted that Friedman and Bigeleisen (2) showed that traces of moisture must be present for ammonium nitrate to decompose below 300°C.

Ammonium Perchlorate. The observed temperature for the crystalline inversion (see figure 13) of ammonium perchlorate agreed with the literature value. In their work, Gordon and Campbell (3) also noted the inversion at 240°C.

Pronounced exothermic decomposition was noted to commence at 375°C rising to a peak at 388°C (see figure 14). As can be seen this peak is in the shape of a plateau with the reaction rate essentially constant over a 10 degree range from about 380°- 390°C. By testing with moistened litmus paper, decomposition was apparent from 275°C on. The litmus was basic (pH 8) from 275°- 375°C becoming strongly acid (pH 2) during the exothermic peak. In their paper Gordon and Campbell (3) did not note any exotherm at 375°C. However, they did get a rapid exothermic peak commencing at 435°C.

Potassium Nitrate. The crystalline transition temperature of KNO_3 (see figure 15) agreed closely with the literature value.

A comparison with other DTA is shown below.

TRANSITION	THIS WORK	GORDON AND CAMPBELL (3)	KRACEK (6)
Rhombic-trigonal	127°C	128°C	130°C

The fusion of KNO_3 commenced at 317°C and reached a peak at 331°C, this latter temperature occurring 6°C below the reported fusion temperature (see figure 16). In their DTA Gordon and Campbell (3) reported fusion at 332°C.

Potassium Perchlorate. The crystalline transition temperature of $KClO_4$ (see figure 17) agreed closely with the literature value. A comparison with other DTA is shown below.

TRANSITION	THIS WORK	GORDON AND CAMPBELL (3)	MARKOWITZ (7)
Rhombic-cubic	299°C	300°C	300°C

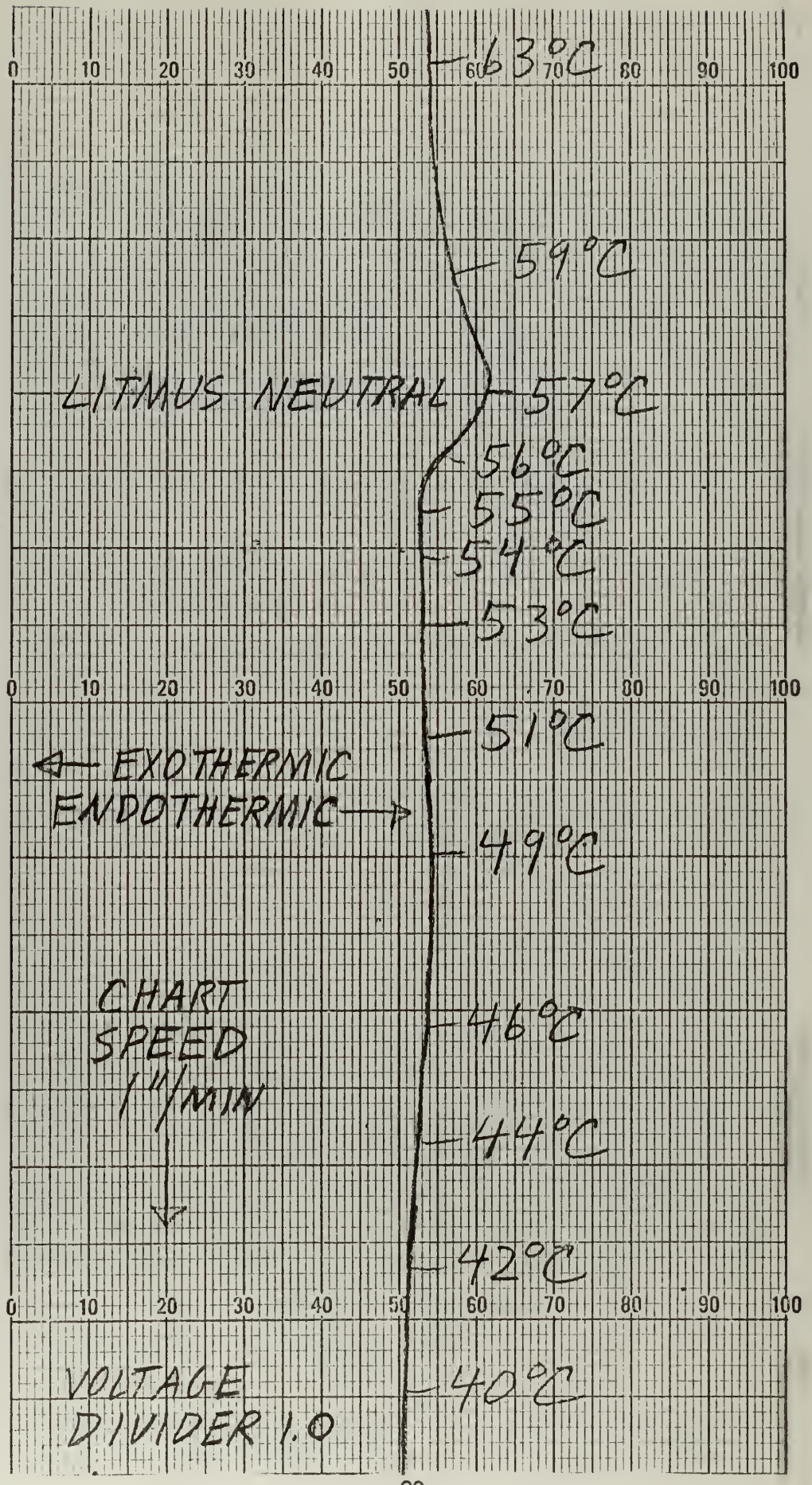

Figure 7 - Thermogram
NH_4NO_3, 40° - 63°C

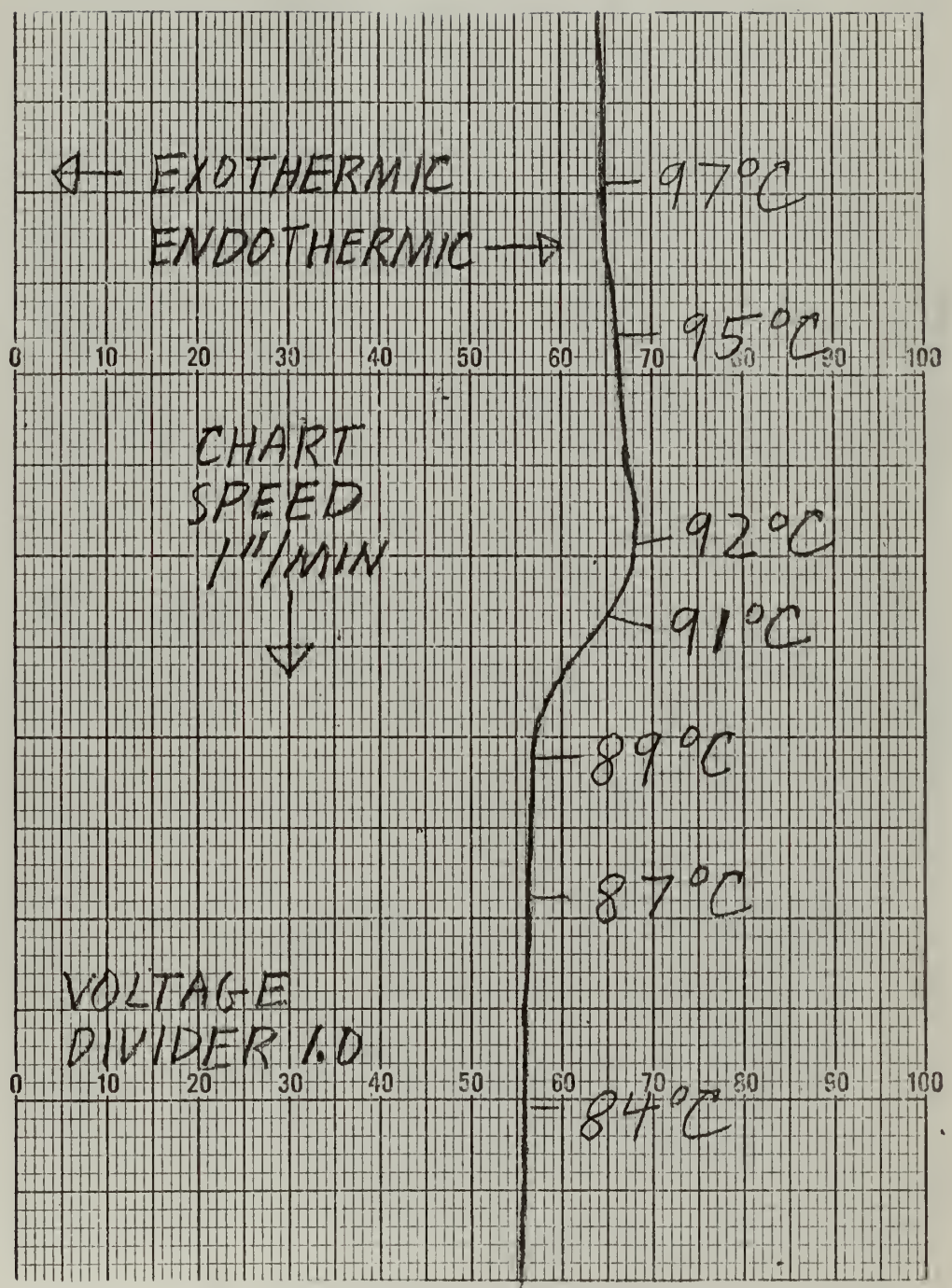

Figure 8 - Thermogram

NH_4NO_3, 84°- 97°C

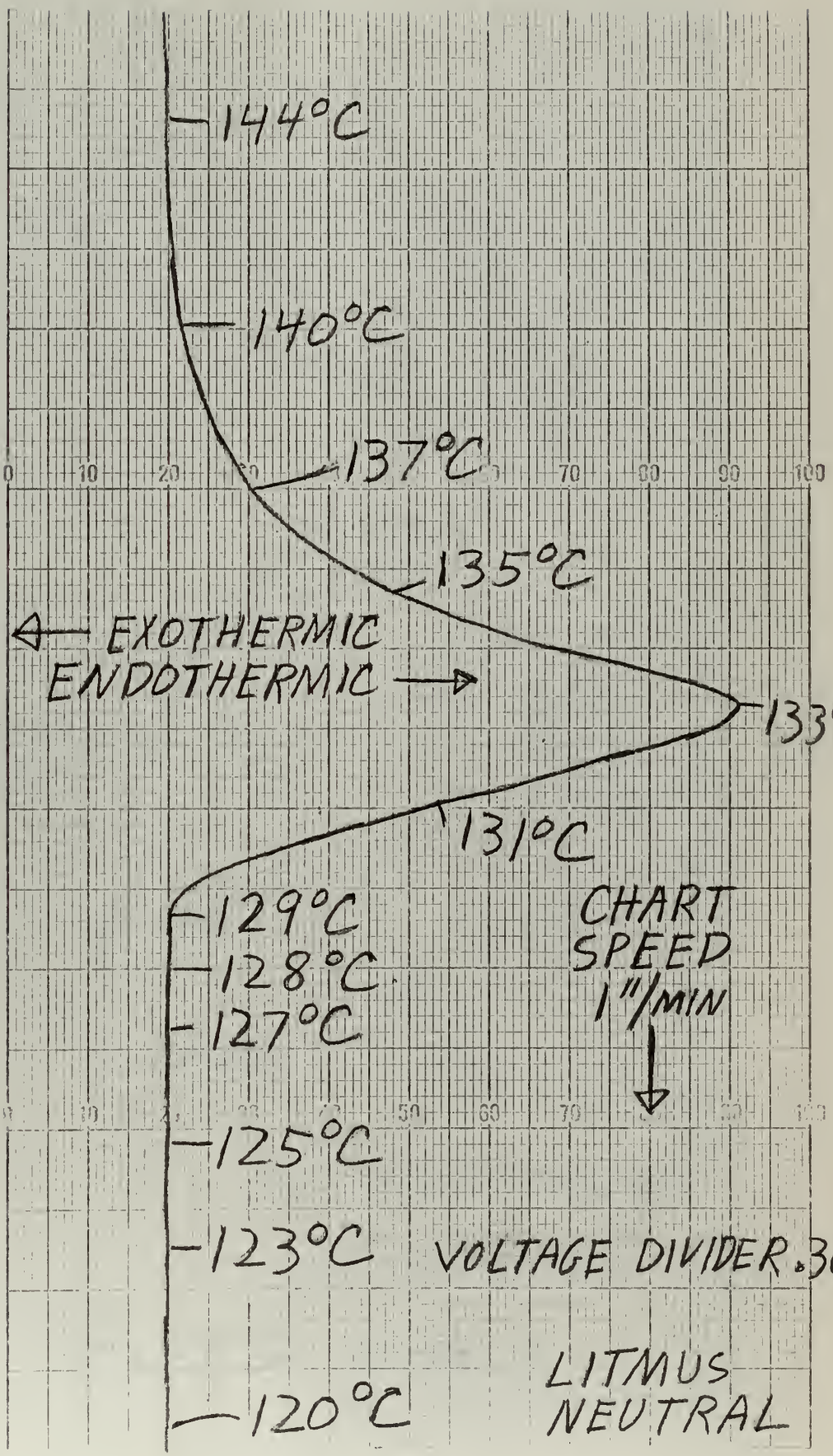

Figure 9 - Thermogram NH_4NO_3, 120° - 144°C

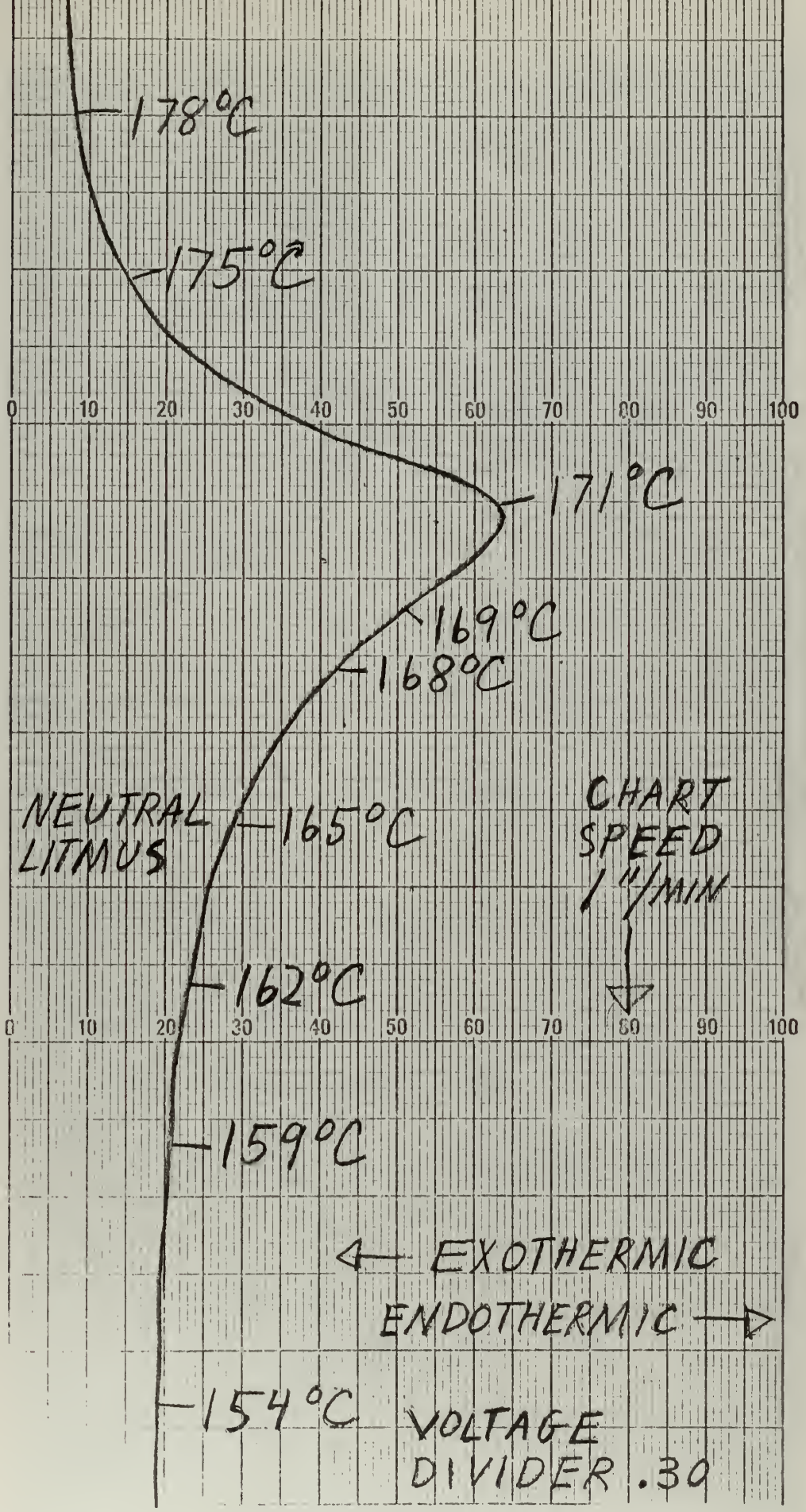

Figure 10 - Thermogram
NH_4NO_3, 154° - 178°C

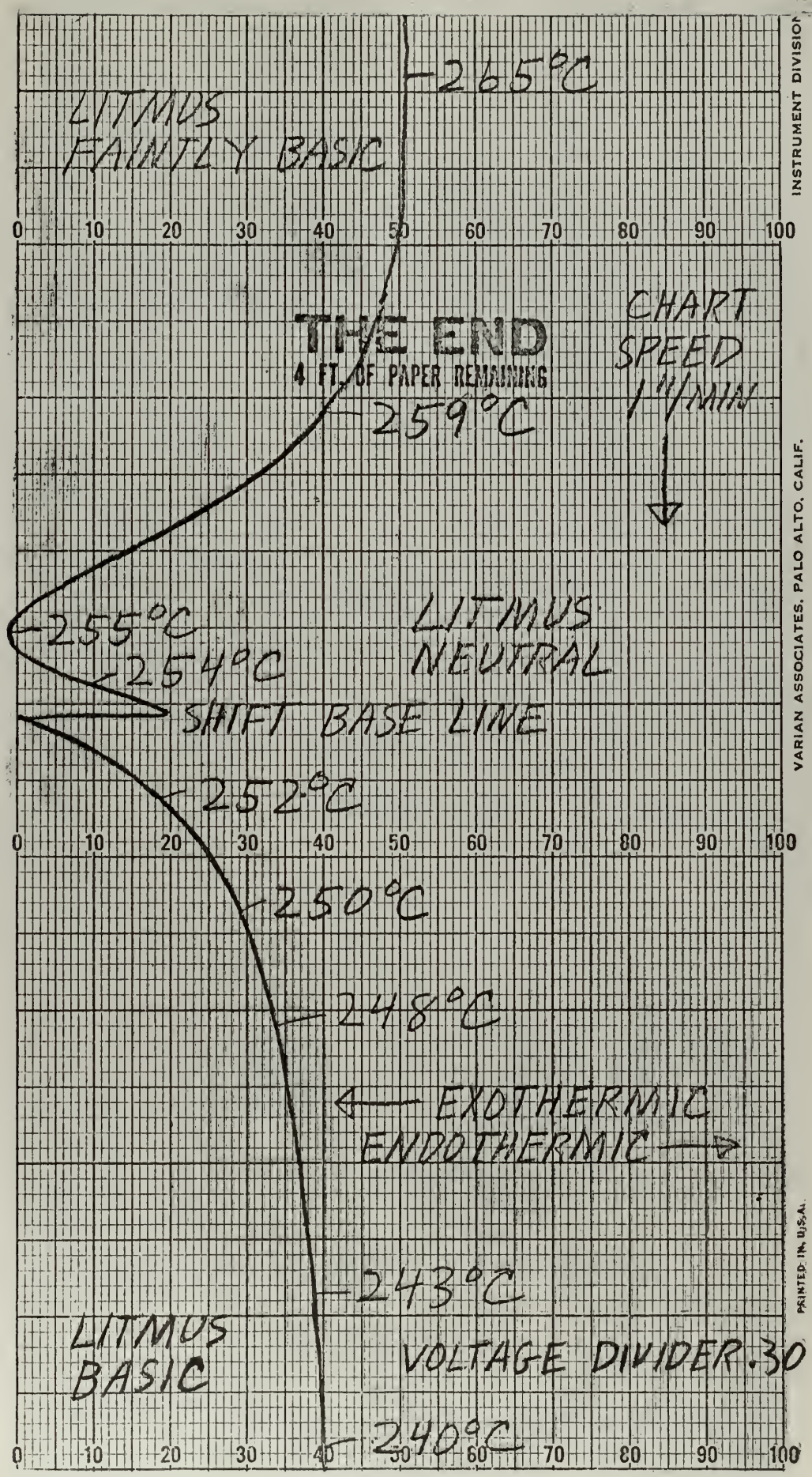

Figure 11 - Thermogram
NH_4NO_3, 240° - 265°C

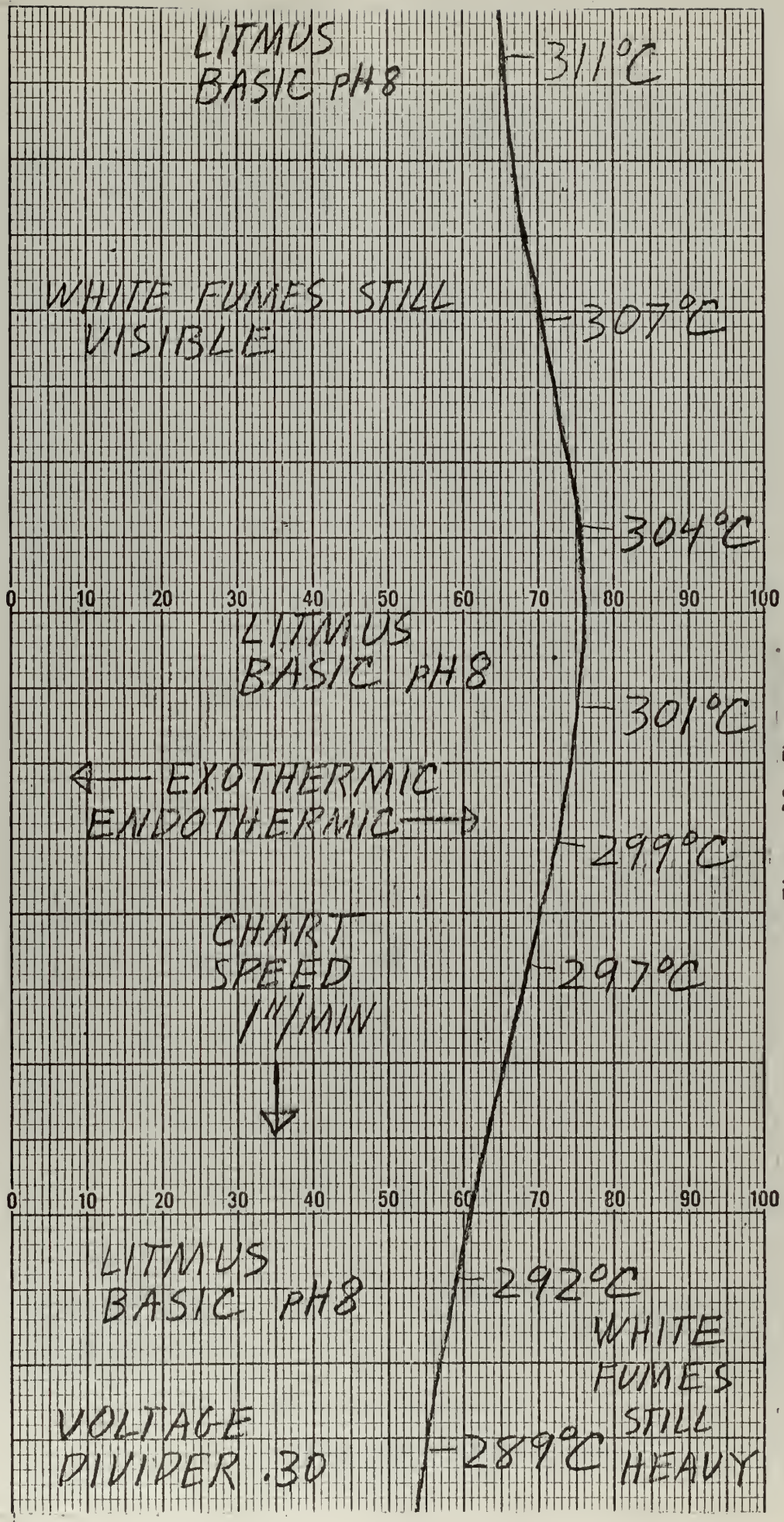

Figure 12 - Thermogram
NH_4NO_3, 289° - 311°C

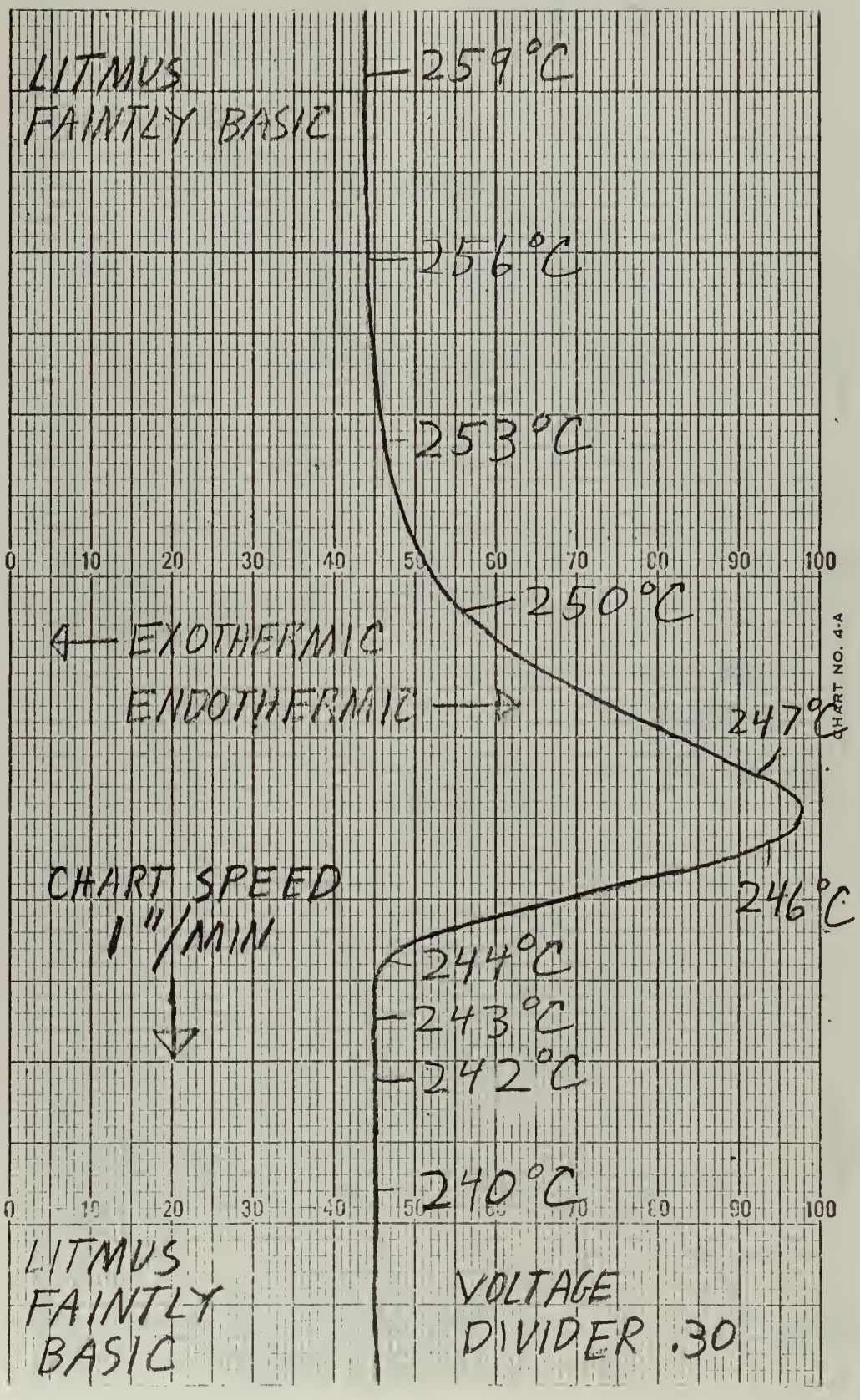

Figure 13 - Thermogram

NH_4ClO_4, 240°- 259°C

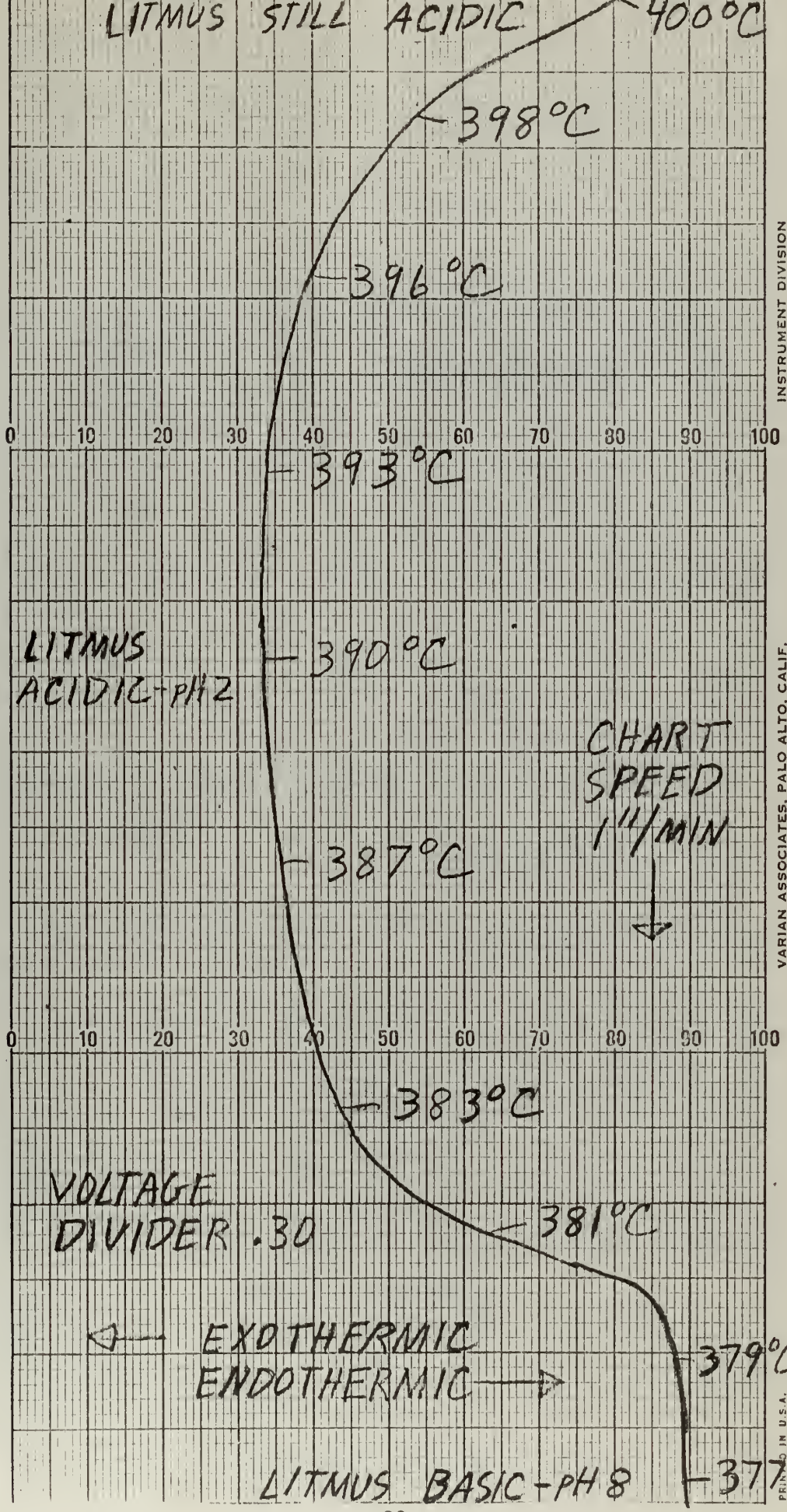

Figure 14 - Thermogram
NH_4ClO_4, 377° - 400°C

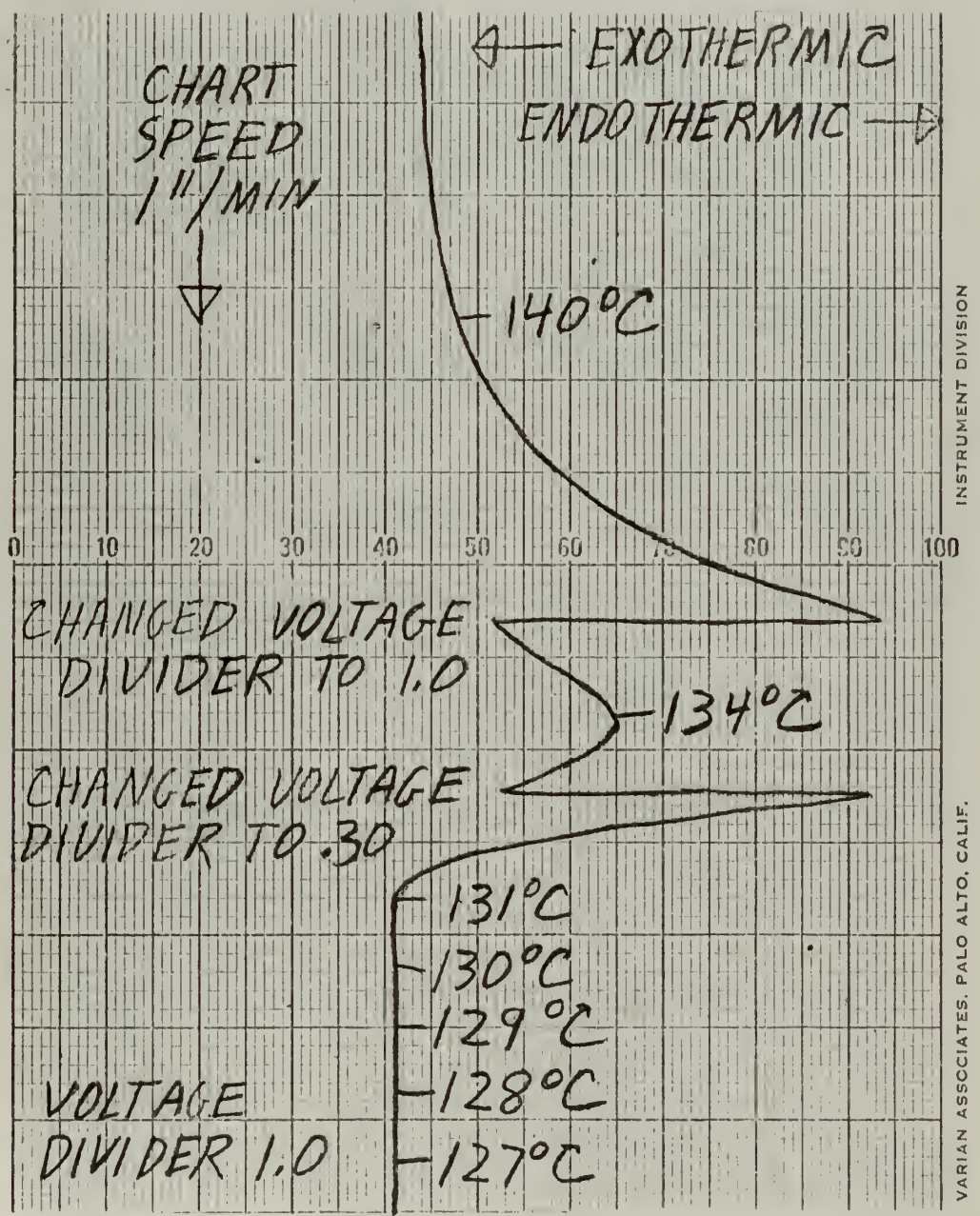

Figure 15 - Thermogram

KNO_3, 127°- 140°C

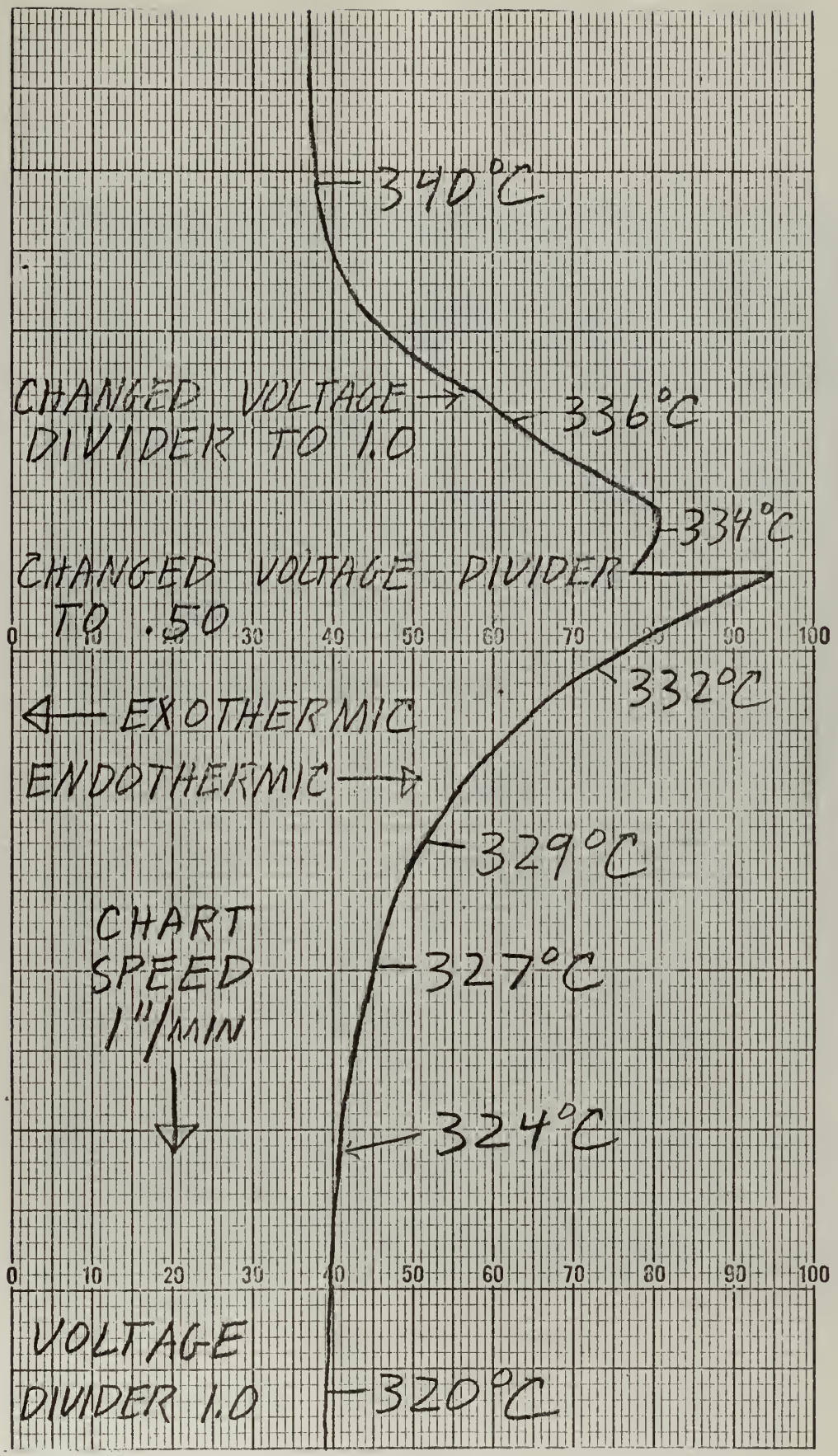

Figure 16 - Thermogram

KNO_3, 320°- 340°C

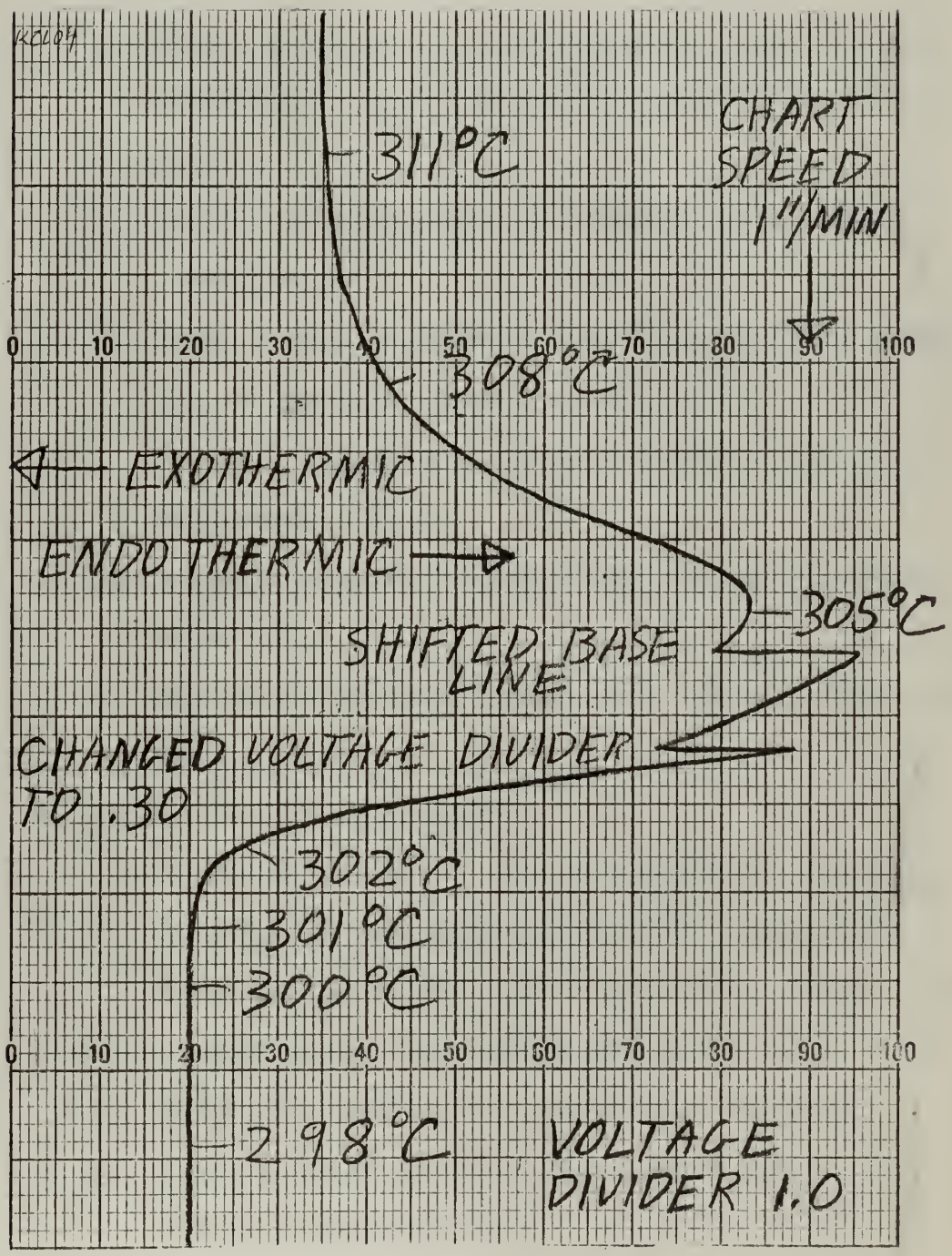

Figure 17 - Thermogram

$KClO_4$, 298° - 311° C

7. Suggestion for Further Work

Suggestions for further work are outlined as follows:

A. Equipment

1. Modify to provide for a more reliable method of taking temperatures, perhaps by use of thermistors or thermocouples.
2. Provide for a continuous and automatic recording of temperature.
3. Modify thermistor probes to provide for complete protection of thermistor leads.
4. Provide a constant D.C. voltage across the bridge independent of load.
5. Calibrate apparatus so that it can be used for quantitative work.
6. Program heating rate to provide for a precise and constant heating rate.

B. Differential thermal analysis

1. Do precise qualitative work on a particular substance, investigating polymorphic changes and decomposition phenomena. A key factor here would be to procure as pure a sample of the chemical as possible.
2. Investigate qualitatively mixtures of reagents.
3. If the apparatus is suitably calibrated make kinetic studies of decompositions.

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